Photoemission Study of a Strongly Coupled Electron-Phonon System

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(Received 2 February 1999)

We present high-resolution photoemission experiments of the $\overline{\Gamma}$-surface state of Be(0001). The spectral function near the Fermi wave vector reveals a strong quasiparticle peak due to coupling with surface phonon modes. The coupling constant λ is estimated to be 1.18 ± 0.07 based on the renormalization of the effective mass. No gap was observed down to 12 K. Any interpretation of the data based on charge density wave formation or surface superconductivity can therefore be discarded.

PACS numbers: 71.38.+i, 71.10.Ay, 73.20.At, 79.60.Bm

It has been recognized for many years that the surfaces of Be have a behavior contrasting the bulk properties of this metal. The electronic structure of Be metal is dominated by the fraction of $2s$ electrons promoted to $2p$ states, leading to severe deviations from the free-electron model. Some examples are an unusually high Debye temperature and Poisson's ratio [1], as well as a large diamagnetic susceptibility and a small electronic contribution to the specific heat [2]. From bulk band structure calculations it is known that the Fermi level is situated in a dip in the density of states [2,3], leading to a number of states at E_F an order of magnitude less than for other simple metals, e.g., Mg [3].

The (0001) surface of Be does not reconstruct, but drastic modification of the bulk properties can be anticipated from the reduction in coordination at the surface. Low-energy electron diffraction (LEED) measurements reveal large deviations of the interplanar spacing at the surface compared to the bulk. Large values for the mean square displacement and thermal expansion are also unveiled [4], and all of these physical parameters are well described by density-functional theory [5]. The surface phonon modes investigated by electron-energy-loss spectroscopy (EELS) could only be reproduced by calculations which assume substantial variations of the nearest neighbor force constants, inducing in the surface layer a reduction of the interplanar bonding and an increase of the in-plane bonding [3,6]. A detailed calculation of the electronic structure of Be(0001) [7] predicts the existence of surface states in gaps of the projected bulk density of states (DOS), in good agreement with angle-resolved photoemission data [8,9]. The charge density originating from the surface states is essentially localized within the first two layers [7,10] and dominates the DOS at E_F by a factor of 4 over the bulk density. As a consequence of the valence charge redistribution, the binding energy of the $1s$ core level, which probes the local charge density [10], is shifted with respect to its bulk value. Four distinct components resolved by x-ray photoemission spectroscopy could be related to emission from layers at different depths below the surface [11]. Finally, the electron inelastic mean free path of 2 Å at low kinetic energies (10–40 eV) is anomalously small compared to about 10 Å of the universal curve due to a high electron-hole pair and/or surface plasmon creation rate [12].

The $\overline{\Gamma}$-surface state of Be(0001) is widely decoupled from the bulk states and forms a nearly ideal two-dimensional (2D) electron gas on a poorly conducting substrate. The almost isotropic parabolic dispersion is fitted with an effective mass which varies between 1.17 [3] and 1.53 [9] times the electron rest mass. The Fermi circle of the surface state has a radius of 0.93 Å^{-1}, corresponding to roughly half the distance $\overline{\Gamma M}$ of the surface Brillouin zone (SBZ). Despite the fact that all these properties are rather well understood within the framework of established theories, a recent scanning tunneling microscopy (STM) study revealed a quite unconventional behavior of this surface state [13]. The surface image obtained for small bias potential shows a complex pattern of electron density waves resulting from scattering at impurities and defects. These so-called energy-resolved Friedel oscillations are now well understood and can be used to map out the dispersion of the surface states involved [14,15]. However, the Be study exhibits two exceptional features: The amplitude of the electron density waves near E_F is huge when compared to observations made on other surfaces [14], and this amplitude decreases dramatically by orders of magnitude for larger bias voltage. Very recently, an electron-phonon coupling parameter of 1.15 was extracted from a photoemission study of the temperature dependence of the surface state linewidth [16]. This value of λ is 5 times the bulk value. The authors claim this to be a possible indication for the existence of surface superconductivity with a high critical temperature [16]. Both the STM and the photoemission experiments suggest the occurrence of a quite unconventional mechanism modifying dramatically the nearly free electron behavior of the surface state near E_F.

The aim of the present study is to investigate whether high-resolution photoemission spectra taken at low temperature can reveal the peculiar nature of the 2D states related to the giant charge oscillations observed by STM, and to test the prediction of superconductivity.

The Be(0001) sample was mechanically polished and cleaned *in situ* by cycles of Ar^+ sputtering at 850 K

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and annealing at slightly lower temperature, with subsequent slow cooling to room temperature. Contamination lines (carbon and oxygen) were barely discernible in Auger spectra recorded with highest sensitivity and a sharp LEED pattern was observed. Our experimental geometry is described in detail in Ref. [17]. The azimuthal orientation of the sample allowed spectra to be taken along the $\overline{\Gamma M}$ line of the SBZ. In order to exploit the energy resolution (5 meV) of our spectrometer, the sample was cooled to 12 K by means of a He flow cryostat. The sharpness and position of the Fermi edge have been controlled on the Ta foil fixing the sample. All spectra presented here have been measured with p-polarized HeI light (21.2 eV), i.e., with the vector potential lying in the mirror plane of bulk Be. The angular resolution is a crucial experimental factor in this type of experiment. For the variable polar angle, where the dispersion is fast, we estimate the resolution to be 0.2°. For electrons emitted from E_F by HeI photons this corresponds to $\Delta k_{\parallel} = 0.007$ Å^{-1}. In the perpendicular direction, tangential to the constant energy curves of the surface state, the resolution is less important and was fixed electronically to 0.5°–1° ($\Delta k_{\parallel} = 0.036$ Å^{-1}).

At $\overline{\Gamma}$, the surface state was measured at a binding energy of 2.73 eV, with a full width at half maximum of 400 meV at 300 K, in agreement with results of previous studies [9,16]. Within our experimental accuracy, the measured dispersion curve $E(k_{\parallel})$ of the surface state is unaffected by the sample temperature in the range 12–300 K [18]. This allows a direct comparison of equivalent spectra recorded at different temperatures.

Figure 1 shows a set of data in a narrow k range near the Fermi level crossing. The relative intensities are normalized to the measurement time, and spectra are numbered for the sake of simplicity. They are labeled by their wave vector with respect to k_F, calculated from the emission angles using a work function of 5.1 eV [7]. From the bottom of the figure, the first two spectra, Nos. 1 and 2, have the expected form and evolution for a surface state moving toward E_F. This trend can still be recognized in the following two spectra, Nos. 3 and 4, but a new weak structure emerges around 60 meV. The relative intensity of this new feature becomes important in the next spectrum, No. 5, and finally dominates completely the spectral function at k_F (No. 6), obtained from the extrapolation of the full dispersion curve of the conventional surface state. This extrapolation is allowed since an isotropic Fermi surface is not altered by interactions [19]. For wave vectors larger than k_F (Nos. 7–10), the peak remains pinned at E_F with a rapidly decreasing intensity.

In order to better characterize the narrow peak, we measured spectra with maximum resolution in energy and angle in the small energy range of 140 meV (Fig. 2). These data clearly show the weak dispersion reaching E_F in the spectrum No. 6. For $k > k_F$, the line shape

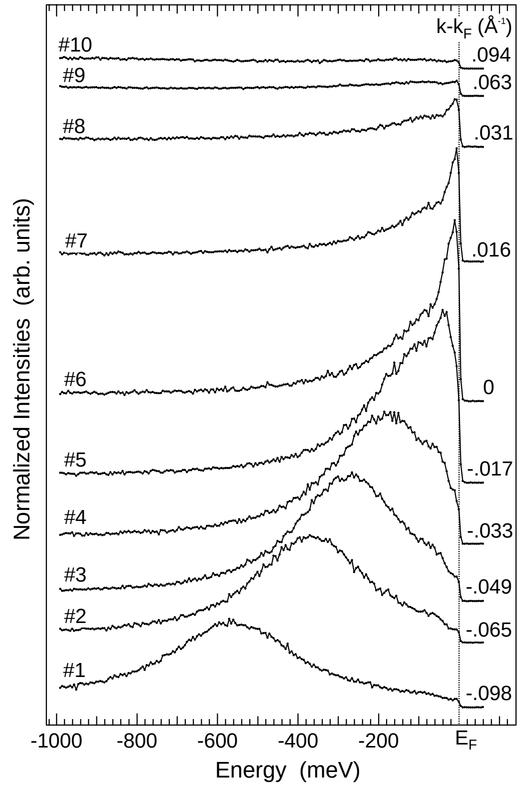

FIG. 1. Photoemission spectra of the Be(0001) surface state near k_F, taken with p-polarized HeI photons (21.2 eV) at 12 K along the $\overline{\Gamma M}$ line of the SBZ. The spectra are normalized to the measurement time; wave vectors, corresponding to emission from the Fermi level, are given with respect to k_F. The numbers are referred to in the text. The angular difference between neighboring spectra is typically 0.5°.

remains unchanged, whereas the amplitude decreases and an intensity excess above E_F is observed (No. 7). The true peak position in the spectra at $k > k_F$ cannot be observed due to the cutoff by the Fermi function, but it can nevertheless be anticipated that the excess in intensity above E_F and the shape of the peak indicate that the maximum lies above the Fermi energy. Furthermore, measurements at 300 K [18] clearly confirm the thermal population of a high density of states for these values of k and one can safely conclude that the state crosses E_F. This observation, together with the experimental position and sharpness of the Fermi edge, exclude the existence of a gap at E_F larger than 4 meV at 12 K. Since the spectral function remains basically unchanged at least up to 60 K [18], where a 4 meV gap should be closed due to thermal excitation, the opening of even such a small gap becomes unlikely. Moreover, identical spectra were obtained in the other high-symmetry direction $\overline{\Gamma K}$ (not shown here, see Ref. [18]) so that the existence of an anisotropic gap can be ruled out. The suggestion of superconductivity [16] can therefore be discarded, despite the resemblance of the spectra to photoemission measurements from high-temperature superconductors [20].

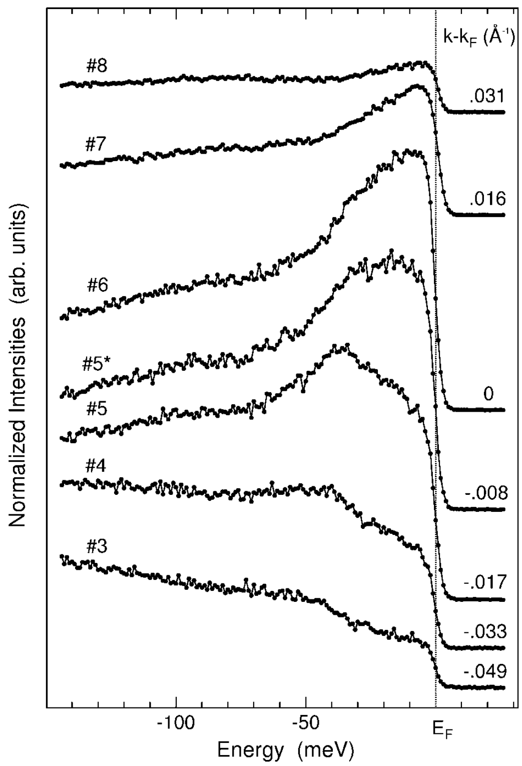

FIG. 2. As in Fig. 1, but taken with maximum resolution in energy and angle (see text). The energy steps are 1 meV; spectra are numbered as in Fig. 1, with an additional spectrum No. $5^{\star}$.

For the same reason, we can rule out an interpretation based on the formation of a charge density wave (CDW), since this requires the opening of a gap. Even if E_F is pinned to the lower band edge, this model is incompatible with our observation of the Fermi level crossing. A further indication of the inadequacy of this mechanism is the lack of extra diffraction spots in LEED images observed at 60 K [21]. Normal emission photoemission measurements on Na thin films yield spectra with an unconventional peak near E_F showing some similarities with our data [22]. The different evolution of the peak intensity and its poorly defined position, limited by the resolution, make any comparison with our spectra hazardous. Surface photoeffect and CDW formation have been invoked to explain the Na data, but this question remains an open controversy [23]. The peak close to E_F that we report here is fully consistent with the STM observation of giant Friedel oscillations on Be(0001) [13]. The small bias voltages ($\leq$35 meV) required to obtain a contrasted STM image establish that only electrons close to E_F are contributing, in agreement with the energy range where this peak is observed in our photoemission spectra. Our data demonstrate that the exceptionally large amplitude of the electron density waves originates from the very low dispersion of this state. Furthermore, one can estimate that the anomalous peak provides a sizable intensity contribution within a range $\Delta k/k_F \approx 0.05$, corresponding to the lower limit of the smearing in the STM image [13].

The electron-phonon interaction is known to profoundly modify the electronic states near E_F in a characteristic energy region of the order of the phonon bandwidth ω_{ph}. Recently, this mechanism has been invoked to explain an anomalous intensity observed in photoemission spectra from α-Ga(010) [24]. For Be(0001), ω_{ph} can be estimated from EELS measurements to about 60–70 meV [6]. This strongly suggests that ω_{ph} sets the correct energy scale for the unconventional line shape evolution observed in our spectra. A many-body ground state results from the electron-phonon interaction and the excitations of this observed with photoemission correspond to the spectral function derived from the initial state by a perturbation treatment [25]. Several years ago, electron-phonon systems were treated within this formalism based on the coupling between an additional electron and phonon modes within the Debye model [26]. These results have been extended to finite temperature and more realistic models, and their relevance in different measurements has been discussed [27]. By taking advantage of the symmetry between electron and hole addition, these spectral functions (e.g., Figs. 14–17 in Ref. [26]) can be compared to our spectra. The agreement between experiment and theory is at least qualitatively quite satisfactory; a sharp peak appears near E_F when the energy of the hole with respect to the Fermi energy becomes comparable to the phonon bandwidth. The quasiparticle picture of the electron-phonon coupling is valid only for energies either very near to or far away from the Fermi energy on the scale of the phonon bandwidth, but it breaks down for $E - E_F \approx \omega_{\text{ph}}$ [26,27]. Close to E_F, this quasiparticle can be more conventionally described as a hole excitation with a mass enhanced by a factor of $(1 + \lambda)$. In order to estimate the mass renormalization factor and, from this, the electron-phonon coupling parameter, it is necessary to compare the dispersion at E_F with that at energies far below. These can be linearized in the small region of interest.

In Fig. 3, the energy positions of the peak maxima are plotted together with the fitted dispersion. Additionally, points extracted from spectra taken at 300 K have been added to emphasize the crossing of the Fermi level. For $k \geq k_F$ these high temperature points were obtained by recording spectra with sufficient statistics in the tail above E_F to allow a subsequent division by the Fermi function. Lines were fitted to the band dispersion for energies $E - E_F > \omega_{\text{ph}}$ and to the renormalized dispersion close to E_F, both shown in Fig. 3. The ratio of the slopes is $(1 + \lambda)$. This yields $\lambda = 1.18 \pm 0.07$, in excellent agreement with the value determined from the temperature dependence of the surface state linewidth [16]. Common values among the elements are mostly smaller than unity (for bulk Be $\lambda = 0.24$), except for some exceptional cases, for example, large gap superconductors like Pb, where λ lies between 1 and 1.6. Our data thus demonstrate that the

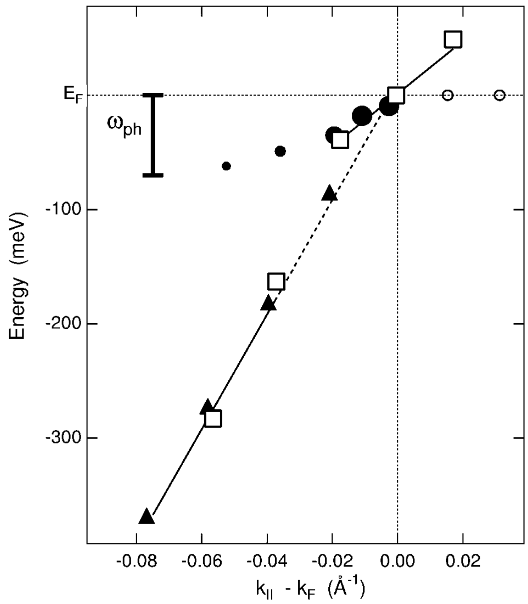

FIG. 3. Energy positions of the peak maxima of the spectra shown in Figs. 1 (solid triangles) and 2 (solid circles) as a function of the wave vector $(k - k_F)$. The remnant feature at E_F for $k > k_F$ is indicated by small open circles. Peak positions taken from spectra at 300 K (open squares) are added. The lines are linear fits to the dispersion of the surface state and the quasiparticle peak. The typical bandwidth of the surface phonons ω_{ph} is indicated.

Be(0001) surface has an individual behavior distinct from the bulk, with a strong electron-phonon coupling at the surface.

In conclusion, we have presented the first unambiguous measurement of the spectral function of a strongly coupled electron-phonon system. The phonon bandwidth sets the correct energy scale for the unconventional line shape evolution observed in our spectra. The linear approximation of the quasiparticle dispersions yields a value of 1.18 for the coupling parameter λ. The evolution of the spectral shape over the Fermi level crossing compares very favorably with theoretical calculations of the spectral function [26,27]. No evidence for a gap opening up at 12 K was found, and consequently, interpretations other than the electron-phonon coupling can be discarded. These results demonstrate the power of high-resolution photoemission in probing the subtle nature of many-body states.

The authors gratefully acknowledge stimulating discussions with R. Frésard, H. Beck, and P. Martinoli. The work was funded by the Fonds National Suisse de la Recherche Scientifique.

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